

"Results of the September 1997 DOE/EPA Demonstration of Multimetal Continuous Emission Monitoring Technologies," P.M. Lemieux, J.V. Ryan, N.B. French, D.B. Burns, W.J. Haas, Jr., and S.J. Priebe, *Waste Management*, Vol. 18, pp. 385-391, 1998.

**RESULTS OF THE SEPTEMBER 1997 DOE/EPA DEMONSTRATION OF
MULTIMETAL CONTINUOUS EMISSION MONITORING TECHNOLOGIES**

P.M. Lemieux and J.V. Ryan
U.S. Environmental Protection Agency
National Risk Management Research Laboratory
Research Triangle Park, NC 27711

N.B. French
Sky+, Inc.
Oakland, CA 94611

W.J. Haas, Jr.
Ames Laboratory
Ames, IA 50011

S.J. Priebe
Idaho National Engineering and Environmental Laboratory
Idaho Falls, ID 83415

D.B. Burns
Westinghouse Savannah River
Aiken, SC 29808

ABSTRACT

In September 1997, the U.S. Department of Energy (DOE) and U.S. Environmental Protection Agency (EPA) co-sponsored a demonstration of several multimetal continuous emission monitors (CEMs). The demonstration, performed at the EPA National Risk Management Research Laboratory, Air Pollution Prevention and Control Division's combustion laboratory in Research Triangle Park, NC, involved the side-by-side testing of seven multimetal CEMs at various stages of commercialization. A series of tests were performed to compare results from the multimetal CEMs to Method 0060, the EPA reference method (RM) for metals emission measurements, using the relative accuracy test audit (RATA) protocol. The EPA operated the test facility and performed the RM sampling, and each multimetal CEM was operated by the instrument's respective developer. To accomplish these tests, an aqueous solution of six toxic metals (arsenic, beryllium, cadmium, chromium, lead, and mercury), along with flyash from a coal-fired utility boiler, was injected into the afterburner of the EPA's rotary kiln incinerator simulator facility to generate a combustor flue gas with realistic post-flue gas cleaning system particulate loadings and target metals concentrations of approximately 15 and 75 $\mu\text{g}/\text{m}^3$, which constituted the low and high concentration test conditions. The multimetal CEMs that participated in the test included two laser-induced breakdown spectroscopy (LIBS) systems, two inductively coupled plasma (ICP) systems, a spark-induced breakdown spectroscopy (SIBS) system, a hazardous element sampling train with x-ray fluorescence (HEST/XRF), and a microwave plasma system. Ten RM-CEM sample pairs were taken at both the low and high concentration test conditions, and the relative accuracies of the multimetal CEMs were calculated. This test provided performance data that will be used to assess the current state of the art in multimetal CEMs.

INTRODUCTION

In theory, multimetal continuous emission monitors (multimetal CEMs) offer an effective way to control pollutants and monitor compliance with emission regulations. Draft EPA regulations¹ provide incentives to use CEMs to reduce waste feed characterization and to reduce dependence on operating parameters for compliance verification. However, multimetal CEM techniques are more complex than CEMs for other pollutants that are already commercially available. Technical risks present serious barriers to commercialization. Of these barriers, performance verification is one of the most important.

This paper describes the third in a series^{2,3} of multimetal CEM performance tests conducted jointly by EPA and DOE. This test was conducted during September 1997 at the Rotary Kiln Incinerator Simulator (RKIS) facility at the EPA National Risk Management Research Laboratory, Research Triangle Park, North Carolina.

This test was designed to measure the performance of multimetal CEMs for regulatory compliance applications. As such, the test focused on six metals currently slated for regulation in the draft EPA Maximum Achievable Control Technology (MACT) rules for hazardous waste combustors:¹ arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), lead (Pb), and mercury (Hg) (note that antimony was dropped from the draft MACT rule during 1997). The most important performance issue is whether the CEMs can quantitatively measure all six metals. To address this issue, two parameters were measured: 1) detectability [at the concentrations tested, compared to required Method Detection Limits (MDLs)], and 2) relative accuracy (RA), which is the average CEM measurement compared to the EPA Reference Method (RM) measurement during the same time period. EPA Method 0060⁴ was used as the RM.

Another important issue when using multimetal CEM data is data scatter. Data scatter is an important consideration because the multimetal CEM is measuring metals that are in both particulate and gas-phase, as opposed to the gas-phase only measurements made by most conventional CEMs. This parameter is more difficult to measure since the actual minute-to-minute variability in trace metals concentration in the process is not known. In addition, data scatter can be a function of both facility flue gas variations and the multimetal CEM technology in question. No National Institute of Standards and Technology (NIST) traceable “metals calibration gas” exists to compare the instruments’ real-time readings to a known source. To try to quantify data scatter, the standard deviation of the data sets during each measurement period is calculated. The standard deviation gives an indication of instrument or measurement temporal variability. By comparing standard deviations of similar data sets from all the CEMs, it is possible to speculate which instruments show higher measurement uncertainty. The purpose of these tests was to operate the facility in such a manner as to minimize concentration variabilities.

Results will be used from this test to speculate which performance specifications in the draft MACT rule are achievable, and which may not be. A technical basis will be provided for decisions on long-term performance testing of multimetal CEMs, which is required before use as a regulatory compliance instrument.

EXPERIMENTAL

Multimetal CEMs Tested

Seven multimetal CEMs were tested. Of these, two are “commercially available” (although with very limited field experience) and five are prototypes under development by research laboratories. Table 1 lists the technology, developing organization, and sponsors for each CEM participant. The eighth participant, Laser Diagnostics, Inc., tested only data analysis software, post-processing Sandia’s raw spectroscopy signal to calculate metal concentrations of their own.

Test Procedures

Testing was performed in the EPA’s pilot-scale RKIS facility (see Figure 1). The seven CEMs were tested side by side in a long duct following the secondary combustion chamber in the RKIS. Two different concentrations of six toxic metals were introduced into the incinerator – approximately 15 and 75 µg/dscm of As, Be, Cd, Cr, Pb, and Hg (note, antimony was not reported because it was recently dropped from the metals regulated in the draft MACT rule). These concentrations were chosen to be close to emission standards in the draft MACT rule and the estimated Method Detection Limits (MDLs) required of a CEM for regulatory compliance purposes.

Test procedures focused mainly on collecting data for RA calculations. These calculations work best with at least nine independent data sets (a data set being the average CEM measurement during a time period when EPA RMs are being sampled). These tests were structured to collect 10 RM samples at each of the 2 different metal concentrations, for a total of 20 RM samples.

The metals were introduced into the flue gas at a steady rate by injecting and atomizing an aqueous metal solution directly into the incinerator’s secondary combustion chamber’s afterburner flame. Flyash particles (taken from a coal-fired utility boiler) containing metals and other inorganic elements were also entrained in an air stream and injected into the incinerator prior to the secondary combustion chamber to simulate flue gas particulate loadings typical of those found downstream of a particulate control device. The additional elements present in the flyash provided potential spectral interferants that would be representative of field operation. No hazardous or other waste was fed into the incinerator during the tests. EPA RM measurements were made at two locations in the duct, one near the upstream CEMs and one near the downstream CEMs.

RESULTS

Table 2 lists the average measurements made by the CEMs compared to the average of the RM measurements. Table 3 lists the RA calculation results for the various CEMs.

Results from these tests show that no CEMs met performance specifications in EPA's draft MACT rule for hazardous waste incinerators during these tests. Only one of the CEMs tested was able to measure all six metals at concentrations tested. Even so, the RA of this CEM varied between 35 and 100%, not 20% or less as required in the EPA performance specification. Because of these observations, it is the authors' conclusion that no multimetal CEM is ready for long-term performance validation for use in compliance monitoring applications given the current performance specifications required for that purpose. Since sampling and measurement of Hg is a consistent problem for multimetal as well as dedicated Hg CEMs, it is suggested that developers of the leading technologies participate in an upcoming DOE-sponsored workshop to solve these and other common CEM measurement issues.

So far, only relative accuracy has been examined, which compares only *average* CEM results to the results of RM measurements. It is also useful to appreciate the discrete nature of the CEM measurements. Each relative accuracy comparison represents the average of tens or hundreds of data points. When the CEM data are plotted as concentration versus time, it can be seen how the discrete data points vary during the averaging time.

Even though data variability is not addressed in the draft EPA MACT rule CEM performance specifications, it will be important if CEM measurement results are to be used for establishing regulatory compliance or for process control. Because of the lack of methods to characterize short term variations in metal concentrations in the duct or stack, it is not known how much of the variation displayed by the CEM results is due to the instrument versus how much is characteristic of the gas stream being measured. Figure 2 shows real-time chromium concentration results for six of the seven CEMs tested, as a function of time, for the first test day. To equitably compare the variability of the results from the different CEMs, 90 seconds was adopted as a standard data averaging and reporting period, and the individual data points were re-averaged from each of the CEMs to periods of that length.

Figure 2 shows that the variability is considerably different for each instrument. In addition to reporting concentrations several times larger than the results of the RM measurements, the Sandia LIBS and PSI SIBS systems showed the most variability in real-time data. The Dial LIBS results also had a more variability than those of the other CEMs. The Navy/TJA, Dial ICP, and MIT MIPS results had the smallest real-time variability.

The standard deviation of the real-time data during each RM measurement period provides a measure of variability. Figure 3 shows standard deviations for CEM data taken on the first test day,

The total length of the error bar is 2 standard deviations. The average of the standard deviations for the CEM data acquired during those RM measurement periods is shown as an error bar on the average concentration for each CEM. The horizontal line in Figure 3 is the average concentration measured from the five RM measurements made that day.

As can be seen from Figure 3, 90-second-averaged data from the CEMs would likely not be very useful for process control or compliance -- assuming catastrophic events such as baghouse failure are monitored using other rapid-response instruments such as pressure gauges. It appears that the characteristic time for changes in emissions in this incinerator is longer than the 90-second averaging time, perhaps on the order of many minutes. Future data from PM and multimetal CEMs should be able to substantiate this hypothesis. In addition, the performance observed for the HEST/XRF technique, although not strictly a CEM (sampling continuously but only analyzing daily or weekly), suggests that a semi-continuous analyzer may have practical applications.

CONCLUSIONS

This test provided performance data that can be used to assess the current state of the art in multimetal CEMs. These data, and the analyses presented in this paper and the forthcoming final report, support the following conclusions:

- The Navy/TJA ICP system can measure all six metals. However, the RA of the Navy/TJA system varies from 35 to 100%.
- The HEST/XRF, although it does not analyze in real-time, and DIAL ICP most likely can be adapted to measure all six metals.
- The test results showed that, for the As and Cd emission lines employed and the resolution of the spectrometric systems employed, the LIBS and SIBS systems suffered from spectral interference that prevented simultaneous measurement of As and Cd at the concentration levels of interest. However, the LIBS or SIBS systems could be adapted to measure extractive samples, either as a replacement for the XRF analyzing the HEST sampling filter paper, or in real-time using an extractive measurement cell.
- None of the analyzers tested demonstrated the capability to measure all six metals at or near concentrations tested here with the required RA of 20%; therefore no CEMs appear ready for long-term testing.
- Based on these tests, it is unknown whether RAs less than 20% are achievable with current technology. It is not known whether this is an inherent limitation of the CEMs or a temporary operational problem that exhibited itself during these tests.

- Additional testing with Hg would be useful to isolate the cause of measurement errors between RM sampling/analysis and CEM sampling/analysis.
- Developers do not use the same method to estimate MDLs. Thus, MDLs cannot be compared between different instruments until a common method is used.
- “Batch” monitoring techniques that pre-concentrate samples on filter paper for post-analysis, such as the HEST/XRF system, are simpler and may be less expensive to operate and maintain than a true “real-time” CEM.
- If a new multimetal CEM calibration procedure were developed, it could spawn a new validation procedure that would allow assessment of RA without using the EPA RM. This would reduce the uncertainty in RA assessments due to uncertainties in the RM, and therefore might create a more achievable performance requirement.

REFERENCES

1. U.S. EPA Proposed Rule "Hazardous Waste Combustors; Maximum Achievable Control Technologies Performance Standards (Performance Specifications)," in Federal Register, Volume 61, pp. 17499 - 17502, April 19, 1996.
2. Ghorishi, S. B., W. E. Whitworth, Jr., C. G. Goldman, and L. R. Waterland, "Testing the Performance of Real-Time Incinerator Emission Monitors," EPA-600/R-97-024 (NTIS PB97-142871), National Risk Management Research Laboratory, U. S. EPA, Cincinnati, Ohio, March 1997.
3. Haas, W. J., N. B. French, C. H. Brown, D. B. Burns, P. M. Lemieux, S. J. Priebe, J. V. Ryan, and L. R. Waterland, "Performance Testing of Multi-Metal Continuous Emissions Monitors," U.S. Department of Energy Research and Development Report Number IS-5128, November 1997.
4. U.S. EPA, "Test Methods for Evaluating Solid Waste: Physical/Chemical Methods," EPA SW-846, Method 0060 "Determination of Metals in Stack Emissions," 3rd edition, Revision 2, September 1994.

Figure Captions

Figure 1. EPA Rotary Kiln Incinerator Simulator.

Figure 2. Real-time chromium concentrations for 6 of 7 CEMs tested as function of time during first day of testing, compared to RM results (horizontal bars).

Figure 3. Average cadmium and chromium concentrations measured by each CEM, compared to the average of five reference method measurements taken on Test Day #1 (9/22/97). Error bars on CEM data indicate the average of standard deviations during each reference method time period.

Table Captions

Table 1. Summary of multimetal CEM technologies, organizations, and sponsors.

Table 2. Average RM and CEM measurements during 10 high concentration and 10 low concentration tests, $\mu\text{g}/\text{dscm}$.

Table 3. Relative accuracy of each multimetal CEM at high and low concentrations.

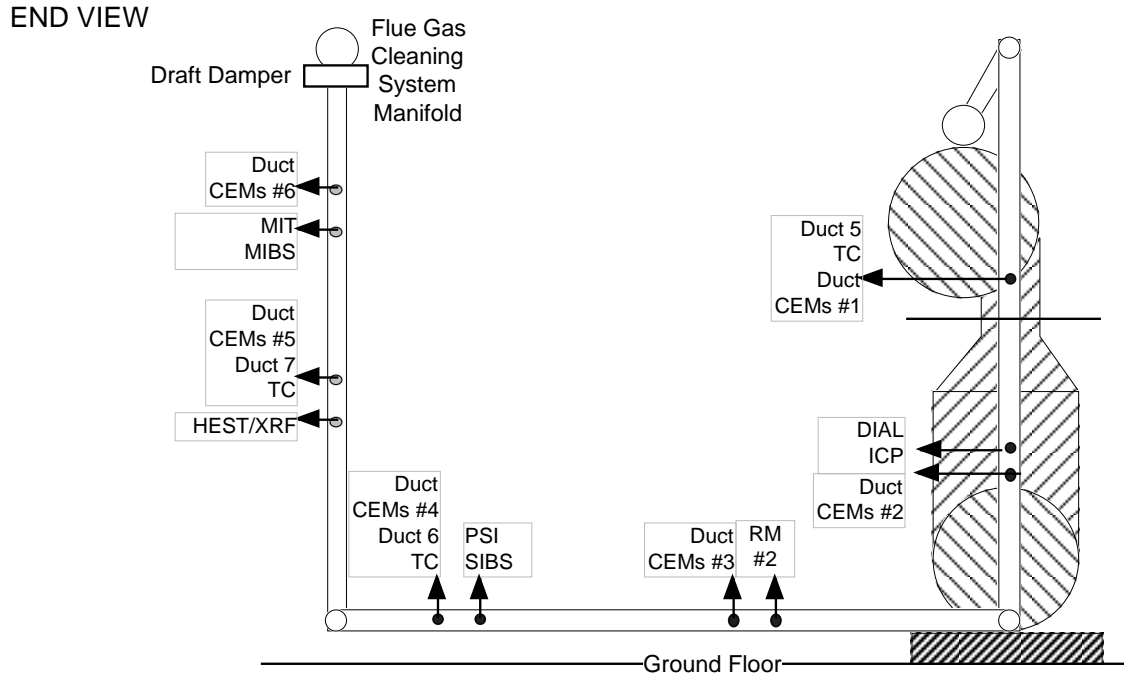
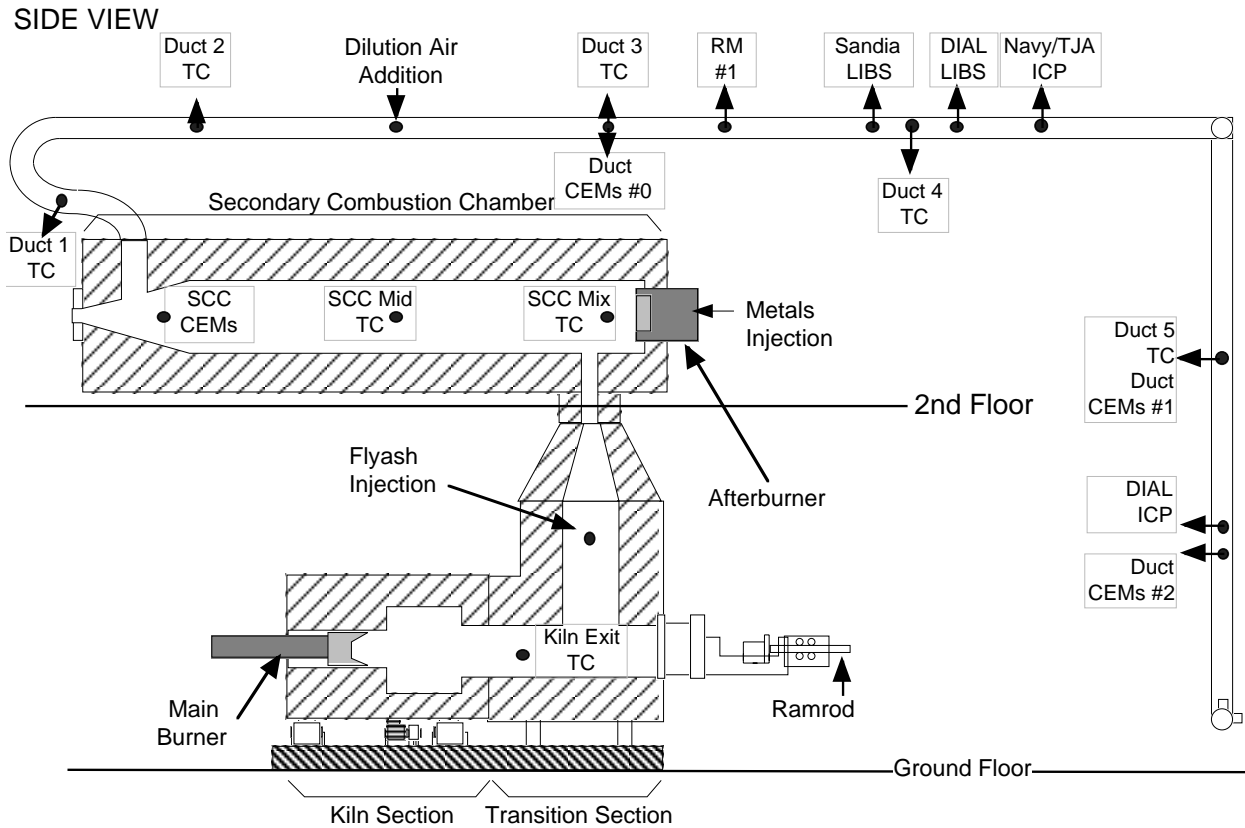


Figure 1. EPA Rotary Kiln Incinerator Simulator

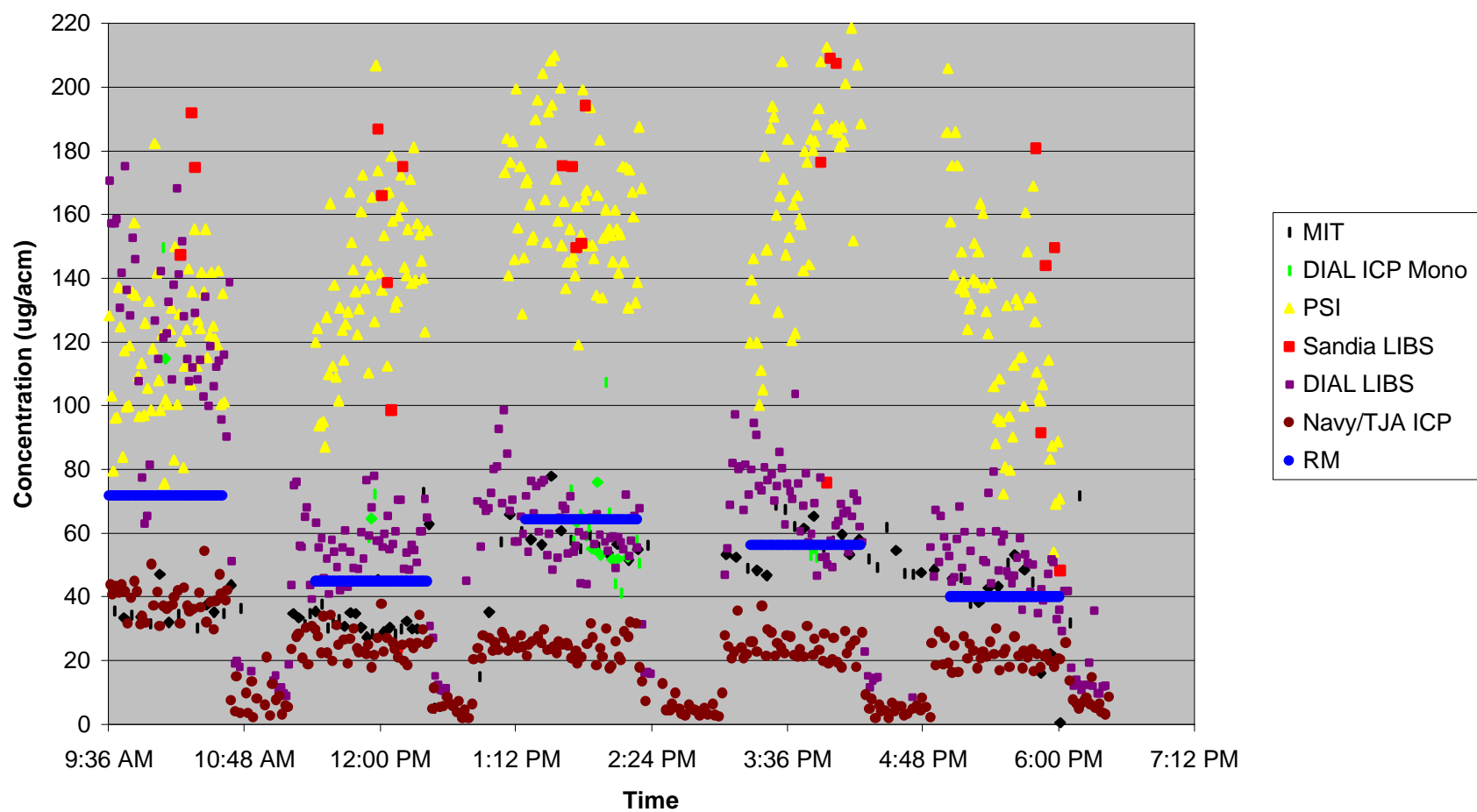


Figure 2. Real-time chromium concentrations for 6 of 7 CEMs tested as function of time during first day of testing, compared to RM results (horizontal bars).

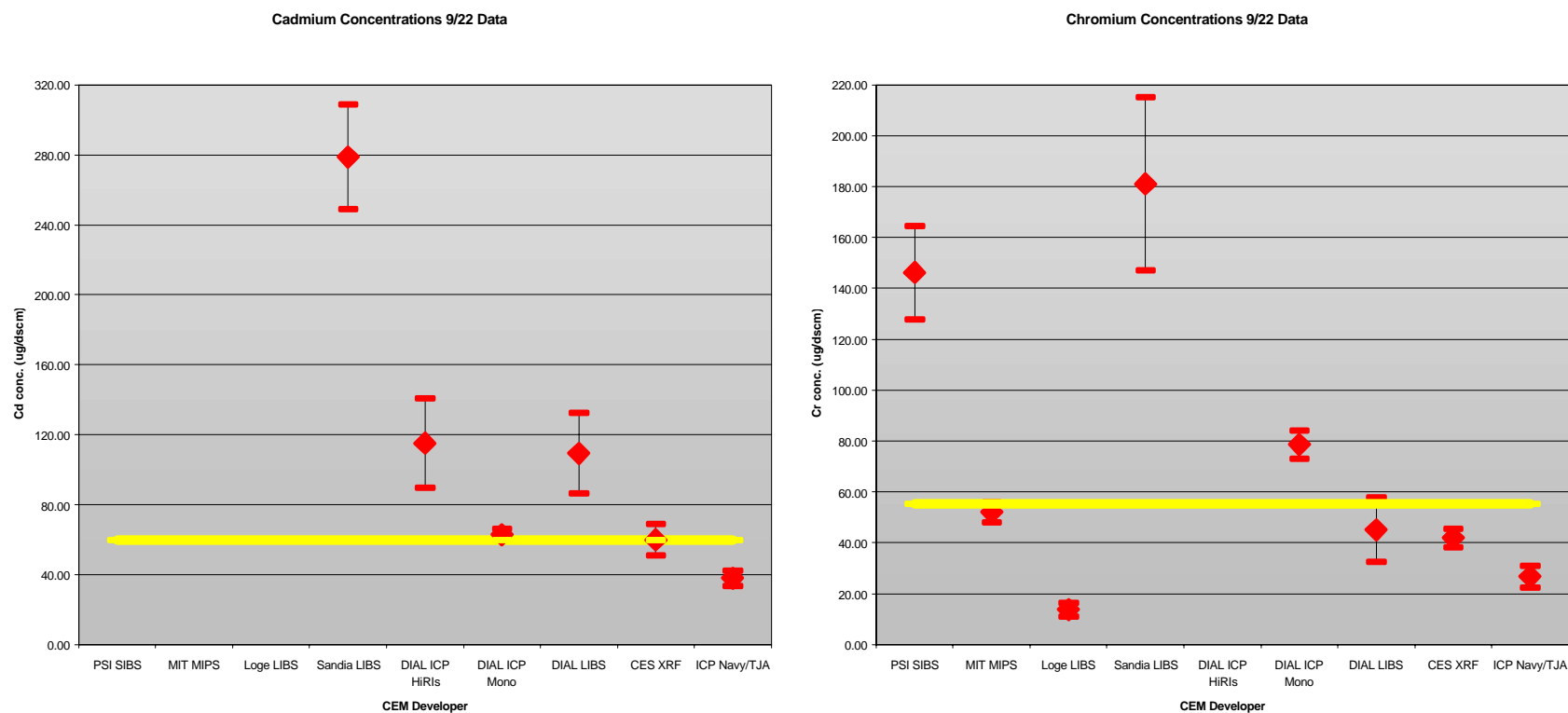


Figure 3. Average cadmium and chromium concentrations measured by each CEM, compared to the average of five reference method measurements taken on Test Day #1 (9/22/97). Error bars on CEM data indicate the average of standard deviations during each reference method time period.

Table 1. Summary of multimetal CEM technologies, organizations, and sponsors

Technology	Developing Organization	Principle of Operation	Abbreviation used	Sponsoring Organization
Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES)	U. S. Department of Defense (DoD) Naval Air Warfare Center	ICP excites metal atoms; quantitation is based on wavelength and intensity of emitted light (extractive)	Navy / TJA ICP	U. S. Army Demilitarization Technology Office Commercially available through Thermo Jarrell Ash
Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES)	Diagnostic Instrumentation and Analytical Laboratory (DIAL) at Mississippi State University	ICP excites metal atoms; quantitation is based on wavelength and intensity of emitted light (extractive)	DIAL ICP Mono & HiRIS	U. S. DOE Characterization, Monitoring, and Sensor Technology Crosscutting Program (DOE CMST-CP)
Hazardous Element Sampling Train with X-Ray Fluorescence (HEST/XRF)	Private. Cooper Environmental Services, Inc.	Samples caught on filter; offline XRF quantifies metals (extractive)	HEST/XRF	Private. Cooper Environmental Services, Inc. Commercially available through CES, Inc.
Laser Induced Breakdown Spectrometry - Atomic Emission Spectroscopy (LIBS)	DIAL at Mississippi State University	Laser excites metal atoms; quantitation is based on wavelength and intensity of emitted light (in situ)	DIAL LIBS	DOE CMST-CP
Laser Induced Breakdown Spectrometry - Atomic Emission Spectroscopy (LIBS)	Sandia National Laboratories, Livermore, CA	Laser excites metal atoms; quantitation is based on wavelength and intensity of emitted light (in situ)	Sandia LIBS	U.S. DOE CMST-CP and the U.S. Army Demilitarization Technology Office
Spark-Induced Breakdown Spectroscopy	Physical Sciences Inc.	Electric spark excites metal atoms; quantitation is based on wavelength and intensity of emitted light (in situ)	PSI SIBS	U.S. DOE, FETC
Microwave Induced Plasma Spectroscopy	Massachusetts Institute of Technology	Microwave excites metal atoms; quantitation is based on wavelength and intensity of emitted light (extractive)	MIT MIPS	U. S. DOE Mixed Waste Focus Area
Calibration Technique for LIBS	Laser Diagnostics Inc.	N/A	Loge	DOE CMST-CP

Table 2. Average RM and CEM measurements during 10 high concentration and 10 low concentration tests, µg/dscm.

Concentration	Avg. RM meas.	Navy / TJA ICP	HEST/XRF	DIAL ICP Mono	DIAL ICP HiRIS	DIAL LIBS	Sandia LIBS	PSI SIBS	MIT MIPS	Loge
High (Target 75)										
As (32 to 90)	72	40	59							
Be (26 to 83)	62	47		44	16	47	163		56	6
Cr (34 to 78)	62	33	43	38		68	196	125	52	14
Cd (31 to 86)	69	44	70	53	65	92	270			1
Pb (34 to 101)	78	38	58	76		110		25	80	
Hg (104 to 226)	182	23	111	146						
Low (Target 15)										
As (16 to 33)	26	14	19							
Be (11 to 26)	20	14		13	10	16	85		21	6
Cr (17 to 33)	27	15	17	9		29	70	58	18	18
Cd (13 to 28)	21	11	27	8		31	77			0
Pb (15 to 35)	27	12	17	20		33		9	19	
Hg (25 to 53)	38	11	18	16						

Note: Blank cells indicate that no measurement was made at that condition

Table 3. Relative accuracy of each multimetal CEM at high and low concentrations.

Concentration (g/dscm)	Avg. RM	Navy / TJA ICP	HEST/ XRF	DIAL ICP Mono	DIAL ICP HiRIS	DIAL LIBS	Sandia LIBS	PSI SIBS	MIT MIPS	Loge
High (Target 75)										
As (32 to 90)	72	57%	31%							
Be (26 to 83)	62	36%		38%	92%	49%	176%		N/A*	128%
Cr (34 to 78)	62	56%	43%	64%		42%	253%	151%	39%	101%
Cd (31 to 86)	69	49%	22%	40%	84%	67%	341%			ND
Pb (34 to 101)	78	64%	47%	19%		66%		89%	28%	
Hg (104 to 226)	182	96%	53%	43%						
Low (Target 15)										
As (16 to 33)	26	81%	39%							
Be (11 to 26)**	20	51%		46%	55%	37%	367%		37%	91%
Cr (17 to 33)	27	76%	46%	76%		19%	196%	163%	98%	65%
Cd (13 to 28)**	21	86%	55%	84%		78%	290%			112%
Pb (15 to 35)**	27	103%	48%	45%		37%		82%	50%	
Hg (25 to 53)	38	94%	66%	96%						

* Only one CEM measurement for this data set. Relative accuracy is not defined for only one data point in a set.

** Relative accuracies should be measured at close to emission limit. These numbers are lower than emission limit in draft MACT rule, making these relative accuracies not particularly meaningful.